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Phase transition in $TlLiMoO_4$ ceramics

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Abstract : The polycrystalline samples of $TlLiMoO_4$ was prepared by solid state reaction technique. Preliminary X-ray studies have been carried out to check the formation of single phase compound and to determine the basic crystal structure Measurements of dielectric constant (ε) and loss (tan δ) as a function of temperature and frequency and electrical conductivity have shown a dielectric anomaly and a phase transition at about $10 \pm 2°C$

Keywords : Structure analysis, X-ray diffraction, dielectric constant

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1. Introduction

Since the discovery of ferroelectricity in perovskite $BaTiO_3$ in 1945 [1], a large number of pure or complex oxides, in single crystal, ceramics or thin film form, of different structural families have been synthesized and characterized using conventional or advanced experimental techniques in search of new materials for industrial applications [2–6]. Among all the oxide materials studied so far, some lead, rare-earth or alkali ions based molybdates and tungstates [7–10] have been found attractive because of their wide variety of crystal structure and physical properties. It has been found that some molybdates and tungstates of tridymite and cristobalite structural families with general formula $ABXO_4$ (where A and B = univalent large and small size cations respectively, X = W, Mo) have multiple or successive phase transition from high temperature cubic phase (point group m3m) to low temerature monoclinic phase (point group m) [11,12]. Because of large variation in ionic size, disorder in oxygen atom or tetrahedral group, a lot of distortion in the above family members have been observed [13]. In view of the above importance and for the better understanding of the phase transition in this family, we have carried out the systemetic studies on structural, electrical and spectroscopic properties of $A^+B^+X^{6+}O_4$

compounds, on which only a few reports are available. In this paper, we report preliminary structural, and detailed dielectric and electric properties of $TlLiMoO_4$ (hereafter TLM) compounds.

2. Experimental details

Polycrystalline sample of the TLM compound was prepared by the solid state reaction techniques using high purity Tl_2CO_3 (99%, Aldrich Chemical Co., USA), Li_2CO_3 (99%, s.d. Fine Chemical Pvt. Ltd.) and MoO_3 (AR grade, BDH, England). Stoichiometric mixture of these carbonates/oxide was thoroughly mixed in an agate mortar for 3h and then calcined at 600°C for 10h in natural atmosphere. The cooled material was again powdered and recalcined at 600°C for 10h to get the required material. The formation of the prepared material was checked by X-ray diffraction technique.

From the fine homogeneous powder of the TLM, pellet samples (diameter 10.9 mm and thickness 1–2 mm were prepared using polyvinyl alcohol (PVA) as a binder, by cold isostatic pressing at 6×10^7 kg/m^2 using a hydraulic press. The pellets were sintered at 650°C in normal atmosphere for 12h. The density of the sintered pellets was determined to be 6.66 gm/cc. X-ray diffraction technique was used to check the quality and formation of the material. The diffractogram (XRD) was recorded at room temperature in a Philips (PM 9920) diffractometer using CuK_α (λ = 1.5418 Å) radiation in a wide range of Bragg angle ($20° \leq 2\theta \leq 100°$) at the scanning rate of 2°/min. For dielectric measurements, the sintered pellets were polished with fine emery paper to make both the surface flat and parallel. Conducting silver paint was applied to both the faces of the samples for better contacts. Measurements of dielectric constant (ε) and loss (tan δ) were carried out using a GR 1620 AP capacitance measuring assembly as function of frequency (400 Hz to 10 KHz) at room temperature and as a function of temperature (from –70°C to 100°C) at 10 KHz in conjunction with a laboratory built three-terminal sample holder. The dc resistivity of the sample was measured as a function of electric field (10–40 v/cm) and temperature (RT-320°C) using a KIETHLEY-617 programmable electrometer.

3. Results and discussion

The sharpness and the singlet reflection peaks of the XRD profile of calcined powder (at 600°C) [Figure 1] support the formation of single phase compound. All the reflected peaks of the calcined powder were indexed from their observed d-values and cell parameters of the compound were determined in different cell configurations using a standard computer program package (*viz.* Powder). The best agreement between the calculated and the observed d-values (Table 1) with the orthorhombic cell parameters (a = 10.370 Å, b = 11.3067 Å, c = 15.7690 Å) suggests the correctness of the preliminary crystal data and the crystal structure of the compound at room temperature. The linear average particle size (P)

of the TLM sample was calculated from X-ray profile using strong and middle intensity peaks with Scherrer's equation

$$P = \frac{0.89\lambda}{\beta_{1/2}\cos\Theta},$$

where $\beta_{1/2}$ = half peak width of the reflection, was found to be 275 Å.

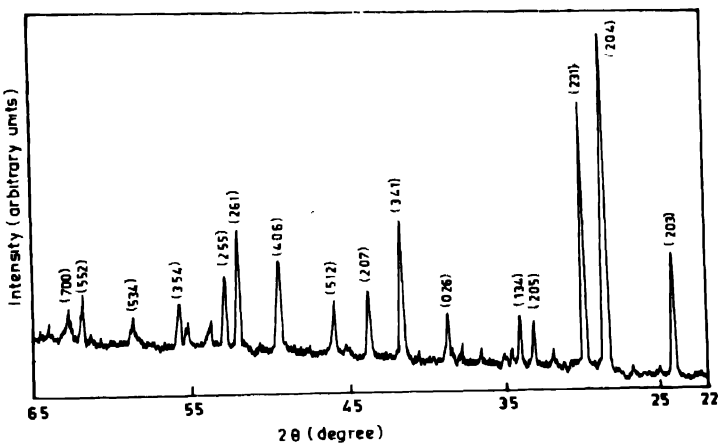

Figure 1. X-ray diffraction patterns of TLM at room temperature.

Table 1. Comparison of some observed and calculated d-values (in Å) of some reflections of TLM at room temperature

$h\,k\,l$	d_{obs} (Å)	d_{cal} (Å)	I/I_0
2 0 0	5.1852	5.1852	7
2 0 2	4.3323	4.3323	6
1 2 2	4.2006	4.2006	8
2 0 3	3.6917	3.6914	34
2 0 4	3.1378	3 1382	100
2 3 1	2 9938	2.9932	76
3 1 3	2.8011	2.7983	7
2 0 5	2 6951	2.6945	14
1 3 4	2.6329	2.6348	15
3 0 4	2.5996	2.5991	6
4 0 2	2.4649	2.4629	8
0 2 6	2.3829	2.3832	6
4 0 3	2.3266	2.3252	15
3 4 1	2 1684	2.1675	39
2 0 7	2.0668	2.0661	20
5 1 2	1.9749	1.9750	16

Table 1. *(Cont'd.).*

h k l	d_{obs} (Å)	d_{cal} (Å)	I/I_0
4 0 6	1.8449	1.8457	25
2 6 1	1 7602	1.7600	33
2 5 5	1.7323	1.7322	20
3 5 4	1.7054	1 7060	7
4 5 2	1 6653	1.6657	6
5 3 4	1.6502	1.6502	14
5 5 2	1 5012	1 5006	15
7 0 0	1 4818	1.4815	10
5 6 0	1 3949	1 3947	15
4 3 9	1.3550	1 3547	16

Figure 2 shows the variation of dielectric constant (ε) and loss (tan δ) of the sample as a function of frequency at room temperature. The nature of variation of these parameters

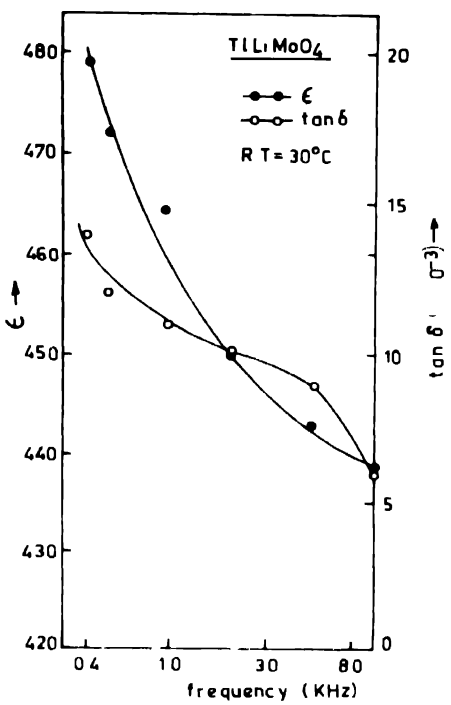

Figure 2. Frequency dependence of dielectric constant (ε) and loss (tan δ) of TLM at room temperature.

show the normal behaviour of dielectrics. Dielectric constant (ε) of TLM decreases significantly with the increasing frequency. This is due to presence of all types of polarisation [14] (*viz.* electronic, dipolar, interfacial, orientational *etc.*) at room temperature and low frequencies. The variation of dielectric constant (ε) and loss (tan δ) [Figure 3] were almost constant at low temperature (–70°C to –15°C) and then increased very fast upto its

maximum value (*i.e.* 1875) at about 10°C. As the temperature increases, the value of ε decreases rapidly after 10°C. This shows the normal behaviour of ferroelectric materials [14].

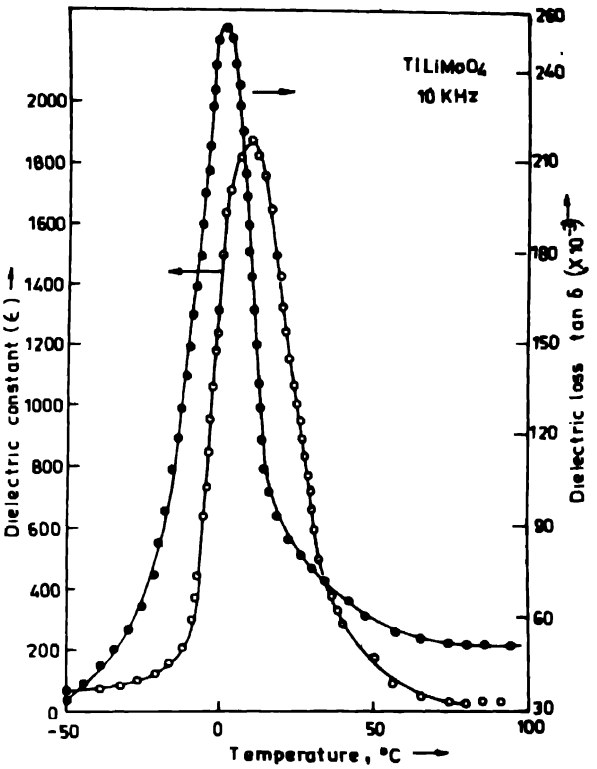

Figure 3. Frequency dependence of dielectric constant (ε) and loss (tan δ) of TLM at 10 KHz.

The diffuseness in phase transition of the compound has been examined by the following formula [15] :

$$1/\varepsilon - 1/\varepsilon_{max} \propto (T - T_{max})^{\gamma},$$

where ε_{max} is the maximum value of ε at T_{max} and γ is an arbitrary constant. The slope of ln $(1/\varepsilon - 1/\varepsilon_{max})$ *vs* ln $(T - T_{max})$ graph (Figure 4) gives the value of $\gamma = 2.1$ which is close to 2 for a typical diffuse phase transition.

The temperature dependence of ac conductivity (σ) and activation energy (E_A) of the TLM sample have been calculated from the dielectric data using the formulae,

$$\sigma = \omega \varepsilon_0 \varepsilon \tan \delta$$

and

$$\sigma = \sigma_0 \exp(-E_A/K_B T),$$

where ε_0 = dielectric constant of free space, ω = angular frequency and K_B = Boltzmann constant [16]. The value of activation energy just below the transition temperature has been found from the slope of the ln σ *vs* $1/T$ [Figure 5] plot. An anomaly in conductivity was

found very near to the transition temperature observed in the dielectric studies. At low temperature, the behaviour of conductivity is very similar to the other group of ferroelectric

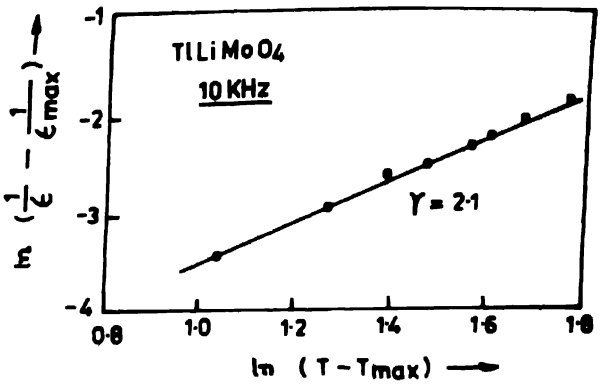

Figure 4. Plot of ln $(1/\varepsilon - 1/\varepsilon_{max})$ *versus* ln $(T - T_{max})$ for TLM at 10 KHz.

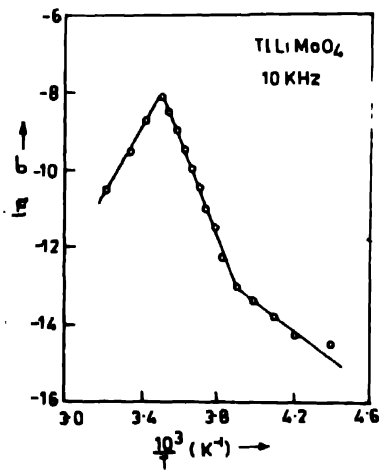

Figure 5. Variation of ac conductivity (ln σ) as a function of inverse of absolute temperature ($1/T$) of TLM at 10 KHz.

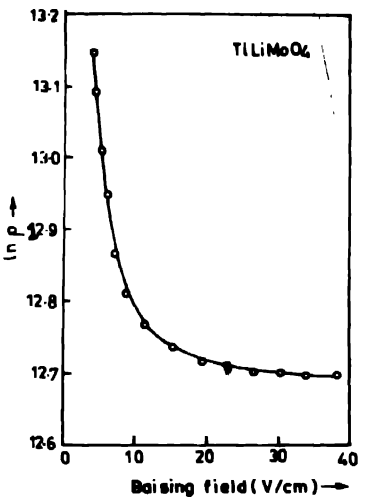

Figure 6. Variation of dc resistivity (ln ρ) as a function of biasing field of TLM at room temperature.

ceramics [17]. The activation energy was 1.46 eV which was connected with the temperature and mobility of oxygen ion vacancies. Figure 6 shows the variation of dc resistivity as a function of biasing field at room temperature. From this curve, it has been found that the dc resistivity decreases with increasing biasing field due to some causes [18] : (a) The gases and moistures present in the pores/cracks of inhomogeneous ceramics are ionized due to application of electric field. The electric field produces the local heat which resulting the generation of thermal stress, can generate cracks, increases the further ionization upto certain field. (b) Electrons ejected from the electrode materials are accelerated through the sample and collide with ions or atoms in the solid, knocking out

other electrons and ionization takes place. So, the resistivity comes down as the biasing field increases. The variation of dc resisitivity as a function of reciprocal of absolute temperature for TLM has been shown in Figure 7. It was found that the resistivity decreases

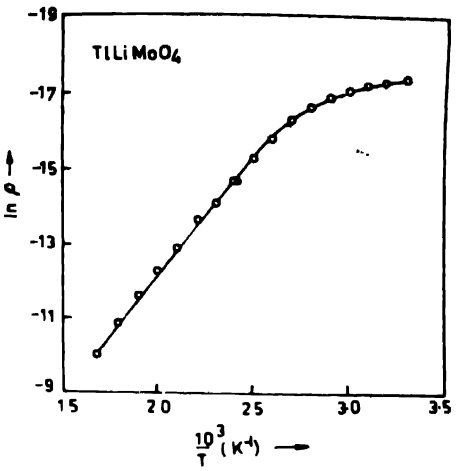

Figure 7. Variation of dc resistivity ($\ln \rho$) as a function of inverse of absolute temperature ($1/T$) of TLM at 40 v/cm

with increasing temperature; one possible explanation may be that the insulators have no free carriers, but were due to thermal energy O_2^- could be set free. The conductivity of the sample increases as the electrons are available in it. So, it is clear that the activation energy of the TLM compound is very small at high temperature and is quite higher compared to the activation energy of its isomorphous compound TLW [18].

Finally, it is concluded that TLM compound has orthorhombic structure at room temperature and normal ferroelectric phase transitions with high dielectric constant which does not fall below 1000 from –2°C to 26°C.

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